Steric versus electronic factors in metallacarborane isomerisation: nickelacarboranes with 3,1,2-, 4,1,2- and 2,1,8-NiC2B9 architectures and pendant carborane groups, derived from 1,1′-bis(o-carborane)

Steric *versus* electronic factors in metallacarborane isomerisation: nickelacarboranes with 3,1,2-, 4,1,2- and 2,1,8-NiC_2B_9 architectures and pendant carborane groups, derived from 1,1′-bis(*o*-carborane) †

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Abstract

Metalation of the [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ dianion with various {$NiPP^{2+}$} or {NiP_2^{2+}} fragments (PP = chelating diphosphine; P = monodentate phosphine or phosphite) leads either to unisomerised 3,1,2-NiC_2B_9 species or to isomerised 4,1,2-NiC_2B_9 or 2,1,8-NiC_2B_9 species, all with a pendant C_2B_{10} substituent. The products [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-dppe-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**1**), [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-dppe-4,1,2-*closo*-$NiC_2B_9H_{10}$] (**2**), [8-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-dmpe-2,1,8-*closo*-$NiC_2B_9H_{10}$] (**3**), [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_3)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**4**), [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**6**), [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$\{P(OMe)_3\}_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**9**) and [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2,2-$\{P(OMe)_3\}_2$-2,1,8-*closo*-$NiC_2B_9H_{10}$] (**10**) were fully characterised spectroscopically and crystallographically, whilst [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4,4-$(PMePh_2)_2$-4,1,2-*closo*-$NiC_2B_9H_{10}$] (**8**) was characterised spectroscopically. Overall the results suggest that an important factor in a 3,1,2 to 4,1,2 isomerisation is the relief gained from steric crowding, whereas a 3,1,2 to 2,1,8 isomerisation appears to be favoured by strongly electron-donating ligands on the metal.

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Introduction

In developing the chemistry of 1,1′-bis(*o*-carborane),[1,2] the trivial name for [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-1,2-*closo*-$C_2B_{10}H_{11}$], we recently [3] described the consequences of metalation of one of the cages (following single-cage deboronation) with both {CoCp} and {Ru(*p*-cymene)} fragments (Cp = η-C_5H_5; *p*-cymene = η-$C_{10}H_{14}$, 1-^{i}Pr,4-MeC_6H_4). With the {Ru(arene)} fragment the kinetic product is the unisomerised [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-(*p*-cymene)-3,1,2-*closo*-$RuC_2B_9H_{10}$], a convenient short form of which may be written as 1-C_2B_{10}-3,1,2-RuC_2B_9, but this readily gives way under mild thermolysis to the isomerised 8-C_2B_{10}-2,1,8-RuC_2B_9 species. Fully analogous compounds are formed with the {CoCp} fragment but depend on the source of the metal unit. Using [$CoCpI_2$(CO)] the product is 1-C_2B_{10}-3,1,2-CoC_2B_9 whereas using $CoCl_2$/NaCp followed by aerial oxidation results in the formation of 8-C_2B_{10}-2,1,8-CoC_2B_9. Although the former does not isomerise to the latter in refluxing toluene, it does so if it is reduced and then reoxidised at room temperature. This perhaps suggests that the basicity of the metal fragment might play a role in the ease and nature of the isomerisation of metallacarboranes, a concept that has some literature precedence.[4]

In this contribution we report the results of metalation of the [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ dianion (Fig. 1) derived by single cage deboronation of 1,1′-bis(*o*-carborane), with {NiP_2^{2+}} fragments (P = monodentate phosphine or phosphite) or {$NiPP^{2+}$}fragments (PP = chelating diphosphine) of differing size and basicity, with particular interest focussing on the nature of the isomerisation (if any) of the metallacarborane cage and the possibility of distinguishing the factors responsible for that isomerisation.

<Fig. 1 near here>

Results and Discussion

The [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ dianion is conveniently prepared *in situ* as its lithium salt by treatment of [$HNMe_3$][7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{11}$] ([$HNMe_3$]**I**) with *n*-BuLi in THF.[3] Reaction between the dianion and [$NiCl_2$(dppe)] (dppe = 1,2-diphenylphosphinoethane) affords, following work-up involving thin-layer chromatography (TLC) on silica, two isolated products, green **1** and red-purple **2**, in moderate yield (Scheme 1). This synthetic approach mirrors that used by Hawthorne and co-workers to prepare single-cage bis(phosphine)nickelacarboranes.[5]

<Scheme 1 near here>

Compound **1** was initially analysed by microanalysis and mass spectrometry, both of which were consistent with the molecular formula $C_{30}H_{45}B_{19}NiP_2$ [crystals grown from CH_2Cl_2 (DCM) and 40-60 petroleum ether (petrol) contain one molecule of DCM of solvation per molecule of nickelacarborane]. The $^{11}B\{^1H\}$ NMR spectrum was relatively uninformative with

multiple overlapping resonances which cannot easily be integrated (this turns out to be a common feature of most of the compounds reported in this paper). In the ^{1}H spectrum there are, in addition to resonances arising from the dppe ligand, two broad resonances typical of C*H*$_{cage}$ signals, one at relatively high frequency (δ 3.08 ppm, assigned to the carborane cage) and the other at relatively low frequency (δ 1.74 ppm, assigned to the nickelacarborane). The latter appears as a doublet, J = 10.0 Hz, confirmed as arising from coupling to a phosphorus nucleus since it collapses to a singlet on broad-band ^{31}P decoupling. That the two P atoms of the dppe ligand are inequivalent is confirmed by the observation of mutual doublets, $^{2}J_{PP}$ = 25.5 Hz, at δ 51.8 and 41.0 ppm in the ^{31}P{^{1}H} spectrum.

Although these data are fully consistent with **1** being composed of {$C_2B_{10}H_{11}$} and {($NiC_2B_9H_{10}$)(dppe)} icosahedral fragments joined by a C–C bond, as expected, they do not define the isomeric nature of the nickelacarborane and consequently a structural study was undertaken. Good quality single crystals were obtained from THF/petrol and, although the crystallographic analysis revealed evidence for both disordered THF and disordered hexane in the lattice, the molecule of **1** is fully ordered.

A perspective view of a single molecule is shown in Fig. 2. The nickelacarborane has a 3,1,2-NiC_2B_9 architecture arising from simple metalation of the open face of the precursor dianion [**I**-H]$^{2-}$ by the {Ni(dppe)$^{2+}$} fragment. Thus compound **1** is [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-dppe-3,1,2-*closo*-$NiC_2B_9H_{10}$] or, in short form, 1-C_2B_{10}-3,1,2-NiC_2B_9. The presence of the bulky carborane substituent on C1 restricts rotation of the {Ni(dppe)} fragment about the Ni3…B10 axis rendering the phosphorus atoms inequivalent in solution at room temperature, as evidenced by the ^{31}P{^{1}H} NMR spectrum. Moreover, the carborane substituent clearly has an influence on the orientation of the {NiPP} unit. It is well-established that the electronically-controlled orientation of {ML_2} fragments in *M*C_2B_9 icosahedra is a function of the number and positions of the cage C atoms in the carborane ligand face;[6] for two adjacent C atoms (as in **1**) the plane through the {ML_2} fragment should lie perpendicular to the vertical mirror plane through the C_2B_9 unit. In **1** the dihedral angle, θ, between the plane through Ni3P1P2 and the plane through B6B8B10 is 61.87(9)º, not the electronically-preferred 90º. In fact, as Fig. 2 clearly shows, the NiPP plane in **1** lies effectively perpendicular to the plane through C1B10B12 so as to minimise steric congestion between the dppe ligand and the carborane substituent on C1. Even then a degree of steric crowding is still observed in that the NiPP plane is bent back from perpendicular to the plane through atoms B5B6B11B12B9 [dihedral angle 10.76(6)º] and Ni3–C1 is significantly longer than Ni3–C2 [2.338(2) *versus* 2.112(2) Å].

<Fig. 2 near here>

Compound **2**, a co-product of **1**, was assumed to be a geometrical isomer on the basis of microanalysis and mass spectrometry. The main differences in NMR spectra are that in **2** the C*H*$_{cage}$ resonance at low frequency in the ^{1}H spectrum, δ 1.90 ppm, is a simple singlet, and a single (singlet) resonance is observed in the room temperature ^{31}P{^{1}H} spectrum, suggesting rotation of the {Ni(dppe)} fragment about the metal-cage axis that is rapid on the NMR timescale. Cooling a solution of **2** in CD_2Cl_2 freezes out this rotation with the singlet at room temperature giving way to mutual doublets, $^{2}J_{PP}$ = 33.2 Hz, at δ 69.6 and 60.6 ppm, at 199 K, the lowest temperature reached. Using the standard coalescence temperature method [7] ($T_{coalescence}$ = 221 K) the activation energy for rotation of the {Ni(dppe)} fragment is estimated to be *ca*. 35 kJ mol^{-1}.

We assume that the metal-phosphine fragment in **2** is able to undergo unrestricted rotation at room temperature because the nickelacarborane cage had isomerised with the carborane substituent moving away from the Ni-bonded face, and a crystallographic study (Fig. 3) confirmed this to be the case. Compound **2** is [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-dppe-4,1,2-*closo*-$NiC_2B_9H_{10}$] or, in short form, 2-C_2B_{10}-4,1,2-NiC_2B_9, *i.e*. the nickelacarborane portion of crowded molecule **1** has undergone a 3,1,2- to a 4,1,2-NiC_2B_9 isomerisation to relieve that crowding (note that the conventional numbering system for metallacarboranes requires the substituted cage C atom to be at vertex 1 in the 3,1,2- isomer **1** but at vertex 2 in the 4,1,2- isomer **2**). That it is likely that compound **2** forms from the initial compound **1** in the synthesis is supported by the fact that repeated chromatography of green **1** always shows a small amount of a faster-moving red-purple band and freshly prepared NMR samples of **1** always show **2** as a minor impurity. Confirmation is provided by the fact that **2** is recovered in 70% isolated yield by heating a solution of **1** in THF to reflux for two hours.

<Fig. 3 near here>

In 4,1,2-*M*C_2B_9 species C2 occupies the lower pentagonal belt of the icosahedron (working down from the metal vertex) and is not directly bonded to the metal atom but the direct C1–C2 connectivity is retained. Such isomers are relatively rare; there are only ten examples [4a,8] of this isomeric form in the Cambridge Structural Database [9] and all but one of these [8e] are formed by isomerisation of an initial 3,1,2-*M*C_2B_9 isomer. Factors contributing to the reason for this isomerisation will be discussed subsequently.

In **2** the {NiPP} fragment is now bound to a CB_4 face. The expected orientation of the metal-phosphine unit is that in which the dihedral angle, θ, between the NiPP and C1B11B12 planes is 90º,[6] whilst in **2** θ is found experimentally to be only 56.67(3)º. Note however that calculations were based on a [L_2*M*CB_{10}]$^{-}$ anion and it may be that in **2** the C atom in the lower belt has some influence on the orientation observed.

The deprotonation of monoanion $\mathbf{I}^-$ followed by reaction with [$NiCl_2$(dmpe)] (dmpe = 1,2-dimethylphosphinoethane) affords, following work-up, a yellow-orange compound **3** in reasonable yield. From microanalysis and mass spectrometry it was evident that the {Ni(dmpe)$^{2+}$} fragment had added to the [**I**-H]$^{2-}$ dianion as expected. The overall appearance of the $^{11}B\{^1H\}$ NMR spectrum of **3** was clearly different to that for **1** and **2** but spectroscopy alone does not define the isomer type to which **3** belongs. Both CH_{cage} resonances appear as singlets in the ^1H spectrum with that for the carborane (δ *ca*. 2.2 ppm) overlapping the signals from the -CH_2-CH_2- bridge of the dmpe ligand. There are two resonances for the CH_3 groups (overlapping doublets in the ^1H spectrum and singlets in the $^1H\{^{31}P\}$ spectrum) and a singlet in the $^{31}P\{^1H\}$ spectrum, together suggesting that at room temperature the Ni(dmpe) unit is undergoing rapid rotation about an asymmetric carborane cage. As was the case with compound **2**, cooling the sample arrested that rotation ($T_{coalescence}$ = 241 K) affording, for **3**, mutual doublets in the $^{31}P\{^1H\}$ spectrum at δ 48.9 and 45.8 ppm, $^2J_{PP}$ = 48.6 Hz. The activation energy for rotation was estimated as *ca*. 38 kJ mol^{-1}.

The structure of compound **3** was established crystallographically (Fig. 4). Although the molecule is partly disordered (only the major occupancies are shown in Fig. 4) the key result of the study is clear; the nickelacarborane cage has isomerised into a 2,1,8-NiC_2B_9 icosahedron, making compound **3** [8-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-dmpe-2,1,8-*closo*-$NiC_2B_9H_{10}$] or simply 8-C_2B_{10}-2,1,8-NiC_2B_9 in short form. In the metallacarborane the {NiPP} fragment adopts an orientation with θ, the dihedral angle between NiP1P2 and C1B9B12 planes, being 78.97(7)^o, close to the expected [6] 90^o.

<Fig. 4 near here>

Summarising the results so far, addition of {Ni(dppe)$^{2+}$} to [**I**-H]$^{2-}$ results in both unisomerised, 1-C_2B_{10}-3,1,2-NiC_2B_9 (**1**) and isomerised, 2-C_2B_{10}-4,1,2-NiC_2B_9 (**2**) products, and **1** is easily converted into **2** with gentle heat, whilst in contrast addition of {Ni(dmpe)$^{2+}$} to [**I**-H]$^{2-}$ results in the differently isomerised 8-C_2B_{10}-2,1,8-NiC_2B_9 (**3**) as the only isolated product. What causes these isomerisations and why do the different chelating diphosphines result in different isomerised products?

Clearly steric crowding between the $C_2B_{10}H_{11}$ substituent on C1 and the diphosphine ligand on Ni3 of an unisomerised 3,1,2-NiC_2B_9 species is likely to contribute to the isomerisation (we have already noted the steric crowding in compound **1**), since the isomerisation moves the carborane substituent down to the lower pentagonal belt. But relief from steric crowding alone cannot account for our results since an unisomerised product (**1**) was isolated with the larger diphosphine dppe (albeit that **1** could readily be isomerised) whereas no such unisomerised species was found with the smaller dmpe. Moreover, since alleviating steric crowding is as

effective in a 3,1,2- to 4,1,2- isomerisation as it is for a 3,1,2- to 2,1,8- isomerisation what is it that determines which isomerisation path is followed?

A relevant factor may be the differing donor/acceptor abilities of the diphosphines. The relatively electron-withdrawing dppe ligand will reduce the electron density at the metal centre and a 3,1,2- to 4,1,2- isomerisation of the nickelacarborane might help stabilise that since a CB_4 carborane face is expected to be a better donor than a C_2B_3 face (note, however, that this does not necessarily distinguish between a 3,1,2 to 4,1,2 isomerisation and a 3,1,2 to a 2,1,8 isomerisation, since the carborane face in *both* isomerised species is CB_4). There are precedents for 3,1,2- to 4,1,2- isomerisations driven by *reducing* the metal electron density; Hawthorne and co-workers showed that 1-e oxidation of the anion $[3,3'\text{-Ni-}\{1,2\text{-}\mu\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_9H_9\}_2]^-$ caused a 3,1,2- to 4,1,2- isomerisation in one cage,[4a] and Stone *et al* have suggested that the dissociation of labile ligands from 3,1,2-PdC_2B_9 species may facilitate an isomerisation to the 4,1,2- form.[8c] On the other hand the dmpe ligand will be relatively electron-donating, and there is literature precedence for an *increase* in electron density at the metal centre facilitating the 3,1,2- to 2,1,8- isomerisation process; Hanusa and Todd [4b] found that 1-e reduction of 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ (Cp = η-C_5H_5) resulted in a 3,1,2- to 2,1,8- isomerisation at relatively low temperature, and we recently demonstrated a similar phenomenon with a 1,1′-bis(*o*-carborane) analogue of this simple cobaltacarborane.[3] We therefore conclude that the electronic properties of the diphosphines may play some part in determining the nature of the isomerisation process. That the effect of the net addition of electron density to a 1,2-*closo*-C_2 icosahedral heteroborane should result in C1–C2 breaking (as observed in the 3,1,2- to 2,1,8-isomerisation) is fully consistent with the LUMO of 1,2-*closo*-$C_2B_{10}H_{12}$ being antibonding between the cage C atoms.[10]

In a related series of experiments we have also metallated the [**I**-H]$^{2-}$ dianion with {NiP_2^{2+}}fragments (P = monodentate phosphine) (Scheme 2). With *cis*-$[NiCl_2(PMe_3)_2]$ the major product is compound **4**. Microanalysis and mass spectrometry were consistent with the expected overall formula $(C_2B_{10}H_{11})$–{$(NiC_2B_9H_{10})(PMe_3)_2$} and NMR analysis suggested an unisomerised 1-C_2B_{10}-3,1,2-NiC_2B_9 architecture, with the presence of mutual doublets ($^2J_{PP}$ = 43.3 Hz) in the $^{31}P\{^1H\}$ spectrum and the nickelacarborane CH_{cage} resonance showing coupling ($^3J_{PH}$ = 10.8 Hz) to one P atom, as was observed in the case of compound **1**. A crystallographic study (Fig. 5) confirmed this assumption, identifying compound **4** as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_3)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$]. There is disorder between vertices 2 and 4 of the nickelacarborane cage [that shown is (just) the major component] but this does not alter the isomer type. The plane through Ni3P1P2 is inclined at 11.74(6)° to that through B5B6B11B12B9 (similar to the situation in **1**) reflecting the crowding between the carborane substituent on C1 and the PMe_3 ligands which prevents {NiP_2} rotation at room temperature.

<Scheme 2 near here>

<Fig. 5 near here>

During chromatographic isolation of **4** a trace amount of a purple band was also observed, isolation and crystallisation of which revealed both purple and colourless crystals. The colourless material was recovered in only sufficient quantity for mass spectrometry (*m/z* 350.3) and the recording of very weak NMR spectra, and discussion of the nature of this species is deferred until compound **7** is described. The purple material, compound **5**, however, was analysed by mass spectrometry, NMR spectroscopy and *X*-ray diffraction. In the ^{1}H spectrum are two broad singlets characteristic of C*H*$_{cage}$ resonances, one of which is at unusually high frequency, δ 6.13 ppm, and two sets of methyl resonances both showing coupling to P. In the ^{31}P{^{1}H} spectrum is a 1:1:1:1 quartet characteristic of P bound to B ($^{1}J_{PB}$ = 145.8 Hz) and a singlet. A ^{1}H-^{31}P HMBC experiment experiments allowed the C*H*$_3$ resonance at δ 1.74 ppm to be associated with the quartet ^{31}P resonance, and that at δ 1.36 ppm to be associated with the singlet ^{31}P resonance.

The diffraction study (Fig 6) rationalises these spectroscopic findings. In the nickelacarborane cage (which is of 3,1,2-NiC_2B_9 architecture) the metal is ligated by one PMe_3 group and one Cl atom, the latter showing H-bonding to the C*H* atom of the carborane substituent on C1 [H2′…Cl, 2.60(2) Å; C2′–H2′…Cl 147.6(15)º; H2′…Cl–Ni3 77.9(4)º], the origin of the high-frequency resonance of the C*H* atom. A PMe_3 group on B8 completes the molecule and thus the trace compound **5** is identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-Cl-3,8-$(PMe_3)_2$-3,1,2-*closo*-$NiC_2B_9H_9$]. A similar single-cage compound, [3-Cl-3,8-$(PPh_3)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$], afforded by the reaction between [10-PPh_3-7,8-*nido*-$C_2B_9H_{11}]^-$ and *cis*-$[NiCl_2(PPh_3)_2]$, has been reported by Hawthorne.[5] We believe that a similar reaction is the origin of compound **5** involving a phosphacarborane anion which is the deprotonated form of the colourless co-product (*vide infra*). One interesting point is that in **5** the nickelacarborane C*H*$_{cage}$ atom appears as a singlet in the ^{1}H NMR spectrum, whereas in the other 3,1,2- species **1** and **4** it couples to one of the P atoms. The fact that in **5** the sole phosphine is *cis* to the C*H*$_{cage}$ suggests that in **1** and **4** the coupling is to the *trans* phosphine.

<Fig. 6 near here>

The outcome of the reaction between [**I**-H]$^{2-}$ and *cis*-$[NiCl_2(PMe_2Ph)_2]$ was very similar to that above. The major product, compound **6**, is a 1-C_2B_{10}-3,1,2-NiC_2B_9 species, specifically [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$], with inequivalent P atoms ($^{2}J_{PP}$ = 39.7 Hz) in the ^{31}P{^{1}H} NMR spectrum and a nickelacarborane C*H*$_{cage}$ which appears as a doublet ($^{3}J_{PH}$ = 14.0 Hz) in the ^{1}H NMR spectrum, presumably from coupling to the *trans* phosphine. The asymmetry of the nickelacarborane cage is confirmed by the observation of four separate resonances for the C*H*$_3$ groups, doublets in the ^{1}H spectrum collapsing to singlets

on ^{31}P decoupling. A crystallographic study of **6** (Fig. 7) is fully consistent with this spectral analysis. There is some disorder between vertices 2 and 4 of the nickelacarborane cage with the major component shown in the Figure. The key features of the structure resemble those of compounds **1** and **4**; the NiP1P2 plane is twisted away from its expected [6] orientation perpendicular to the plane through B6B8B10 [θ = 54.3(6)^o] by the steric demands of the carborane substituent bonded to C1 and also bent back from perpendicular to the plane through B5B6B11B12B9 [by 12.2(3)^o] for the same reason.

<Fig. 7 near here>

Also similar to the reaction between [**I**-H]$^{2-}$ and *cis*-[$NiCl_2(PMe_3)_2$], a minor purple band was also isolated by TLC following the reaction between the dianion and *cis*-[$NiCl_2(PMe_2Ph)_2$] and, again, crystallisation of this afforded both colourless and purple products. NMR analysis of the purple component strongly suggests that it is a direct analogue of compound **5**.

This time the colourless compound, **7**, was isolated in sufficient quantity for complete characterisation. Microanalysis and mass spectrometry are consistent with the formula $C_{12}H_{32}B_{19}P$. The $^{11}B\{^1H\}$ NMR spectrum contains two low frequency resonances typical of a *nido*-C_2B_9 anion,[11] and a $^1H\{^{11}B\}$ experiment revealed evidence for a bridging B-*H*-B atom at δ -1.93 ppm. Finally, there is a single resonance in the $^{31}P\{^1H\}$ spectrum appearing as a 1:1:1:1 quartet (*i.e.* P bound to B) with $^1J_{PB}$ = 148.5 Hz. All these features are fully supported by the results of a crystallographic study of **7** (Fig. 8). The unprimed cage has not been metalated, rather it has a PMe_2Ph group bound at B10 and a μ-H atom between B9 and B10. Thus compound **7** is [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-10-(PMe_2Ph)-7,8-*nido*-$C_2B_9H_{10}$]. Related species have been reported by Zakharkin et al. [12] and Todd et al.[13] With the nature of compound **7** now established we return to the colourless component of the purple band recovered following the reaction between [**I**-H]$^{2-}$ and *cis*-[$NiCl_2(PMe_3)_2$]. Weak ^1H, $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ spectra recorded for this species are all analogous to those observed for **7** and thus we are confident that this earlier colourless product has an analogous structure. This also fits with the envelope centred on *m/*z 350.3 in its mass spectrum. Based on literature precedence,[5] we assume that compound **5** is the result of reaction between the deprotonated form of this species and *cis*-[$NiCl_2(PMe_3)_2$] (*vide supra*).

<Fig. 8 near here>

The reaction between [**I**-H]$^{2-}$ and *cis*-[$NiCl_2(PMePh_2)_2$] gave a different type of product to those obtained using the PMe_3 and PMe_2Ph analogues. Although microanalysis and mass spectrometry are consistent with the only isolatable product, compound **8**, being ($C_2B_{10}H_{11}$)–{($NiC_2B_9H_{10}$)($PMePh_2$)$_2$} [microanalysis assumes 0.5DCM per molecule of **8**, for which there is evidence from ^1H NMR spectra recorded in [$(CD_3)_2CO$], the observation of a single (singlet) resonance in the $^{31}P\{^1H\}$ spectrum implies isomerisation of the nickelacarborane has occurred.

Frustratingly compound **8** could not be persuaded to crystallise but we are confident that the nickelacarborane cage is the 4,1,2- isomer and not the 2,1,8- isomer from the similarity of the $^{11}B\{^{1}H\}$ NMR spectra of **8** and **2** and the dissimilarity of the spectra of **8** and **3** (Fig. 9). We therefore suggest that **8** is [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4,4-$(PMePh_2)_2$-4,1,2-*closo*-$NiC_2B_9H_{10}$].

<Fig. 9 near here>

Compounds **4**, **6** and **8** represent a series of molecules in which the monodentate phosphine ligands are varied from PMe_3 to PMe_2Ph to $PMePh_2$. Compounds **4** and **6** are unisomerised (3,1,2-NiC_2B_9) whilst in **8** the nickelacarborane cage is isomerised to a 4,1,2-NiC_2B_9 form. Clearly, as the series PMe_3, PMe_2Ph, $PMePh_2$ is progressed there is an increase in both the electon-withdrawing capability and the size of the phosphine and this makes it difficult, if not impossible, to know which of these factors is primarily responsible for the isomerisation.

In view of this we have targeted trimethylphosphite, $P(OMe)_3$, as an important ligand in this work. Since $P(OMe)_3$ is smaller than PMe_3 but more electron-withdrawing than $PMePh_2$ [14] its use may help distinguish the relative importance of the steric and electronic properties of the exopolyhedral ligand in the isomerisation process. However, we are not aware of a simple nickel halide bis(trimethylphosphite) compound $[NiX_2\{P(OMe)_3\}_2]$ which could be reacted with $[\mathbf{I}\text{-H}]^{2-}$ to determine if $P(OMe)_3$ effects an isomerisation. The closest species in the literature are the tris(trimethylphosphite) $[NiI_2\{P(OMe)_3\}_3]$ for which a structure is reported [15] but no synthetic details given, and the bis(triethylphosphite) $[NiBr_2\{P(OEt)_3\}_2]$ for which the reverse is true.[16] On the other hand Wallbridge and co-workers have shown that $P(OMe)_3$ will displace tmeda (tmeda = $Me_2NCH_2CH_2NMe_2$) from [3-tmeda-3,1,2-*closo*-$PdC_2B_9H_{11}$] to afford [3,3-$\{P(OMe)_3\}_2$-3,1,2-*closo*-$PdC_2B_9H_{11}$].[17] Again the simple species $[NiCl_2(tmeda)]$ appears to be unknown but a constitutional isomer, $[Ni_3Cl_5(tmeda)_3]Cl$, is well-characterised.[18]

Accordingly, we have followed two approaches to metalation of $[\mathbf{I}\text{-H}]^{2-}$ with a $\{Ni[P(OMe)_3]_2^{2+}\}$ fragment (Scheme 3). Firstly, we prepared *cis*-$[NiBr_2\{P(OMe)_3\}_2]$ in ca. 71% yield, following the method reported for $[NiBr_2\{P(OEt)_3\}_2]$,[16] and added this to $[\mathbf{I}\text{-H}]^{2-}$ in the standard way. Following work-up the purple compound **9** was isolated in modest yield. Following initial characterisation by microanalysis and mass spectrometry, compound **9** was analysed by NMR spectroscopy. The presence of two mutual doublets ($^2J_{PP}$ = 118.2 Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum and a doublet ($^3J_{PH}$ = 10.0 Hz) for the metallacarborane $C_{cage}H$ resonance in the ^{1}H NMR spectrum, the latter collapsing to a singlet on ^{31}P decoupling, indicated a 1-C_2B_{10}-3,1,2-NiC_2B_{10} species by analogy with the spectroscopic features of **1**, **4**, and **6**. The inequivalence of the phosphite ligands in **9** was also confirmed by the observation of two resonances assigned to OCH_3 units in the $^{1}H\{^{31}P\}$ spectrum. These results are fully consistent with the solid-state structure established for **9** (Fig. 10). Thus compound **9** is [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$\{P(OMe)_3\}_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$]. The plane through Ni3P1P2 subtends a dihedral angle of 55.13(12)° with that through B6B8B10 and is bent back from

perpendicular to the plane through B5B6B11B12B9 by 7.83(9)° to accommodate the steric bulk of the carborane substituent. An interesting feature of the structure is the presence of a hydrogen bond between O21 and H2′ [H2′…O21, 2.19(4) Å; C2′–H2′…O21 170(3)º; H2′…O21–P2 106.5(9)º, H2′…O21–C21 120.3(9)º].

<Scheme 3 near here>

<Fig. 10 near here>

Secondly, we have reacted [**I**-H]$^{2-}$ with 0.5 equivalents of [$Ni_3Cl_5(tmeda)_3$]Cl followed by addition of an excess of $P(OMe)_3$. On work-up this affords purple **9** as a minor component but also a new species, yellow compound **10**, as the major isolated product. By microanalysis and mass spectrometry it is clear that compounds **9** and **10** are both $C_{10}H_{39}B_{19}O_6NiP_2$, but spectroscopically they are quite different. In the $^{31}P\{^1H\}$ NMR spectrum of **10** are two overlapping doublet resonances which suggests (by analogy with **1**, **4**, **6** and **9**) that the carborane substituent is on the upper face of the metallacarborane cage, adjacent to the metal fragment. On the other hand, in the ^1H NMR spectrum the lower-frequency cage C*H* resonance (that of the metallacarborane cage, δ 2.23 ppm) appears as a singlet, unlike the doublets in **1**, **4**, **6** and **9** due to ^{31}P coupling.

The issue was resolved by a crystallographic study of **10** (Fig. 11). Compound **10** is [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2,2-{$P(OMe)_3$}$_2$-2,1,8-*closo*-$NiC_2B_9H_{10}$]. Thus the nickelacarborane cage has isomerised to afford a 1-C_2B_{10}-2,1,8-NiC_2B_9 species in which, in contrast to the situation in compound **3**, the C atom of the nickelacarborane *not* bearing the carborane substituent has migrated to the lower pentagonal face. Although not unknown,[19] this is a relatively unusual type of isomerisation for a *C*-monosubstituted metallacarborane and clearly it is not driven by steric crowding. The key structural features of **10** are that the NiP1P2 plane is effectively perpendicular to the plane through C1B9B12 [θ = 84.70(6)°] and slightly bent back from perpendicular to the plane through B4B5B10B12C8 [2.98(5)°], and there is again an H-bond between the carborane substituent and one phosphite ligand [H2′…O23, 2.351(19) Å; C2′–H2′…O23 158.0(15)º; H2′…O23–P2 99.5(5)º, H2′…O23–C23 128.0(5)º].

<Fig. 11 near here>

What do the structures of **9** and **10** infer regarding what drives the 3,1,2 to 4,1,2 and 3,1,2 to 2,1,8 isomerisations? In **9** the phosphite ligands are small (smaller that PMe_3, PMe_2Ph and $PMePh_2$) and strongly electron-withdrawing, and the nickelacarborane cage has *not* isomerised whereas in compound **8** ($PMePh_2$ ligands) it clearly has. This tends to suggest that for a 3,1,2 to 4,1,2 isomerisation relief from steric crowding is a more important driver than is the electron-withdrawing character of the exopolyhedral ligands. We do not believe that the hydrogen bond between O21 and H2′ in **9** is important in preventing isomerisation since there is evidence that it is relatively weak [δ for H2′ is only 4.59 ppm in **9**, not substantially higher frequency than

those in **3** (4.29), **6** (4.00) and **8** (4.13) in which there is no H-bonding] and, moreover, if the H-bonding is retained in solution, it must be fluctional between all three OCH_3 groups on the P2 ligand (since these are equivalent by NMR) which also argues against it being very strong.

In contrast, the 1-C_2B_{10}-2,1,8-NiC_2B_9 architecture of **10** strongly implies that the major influence driving a 3,1,2 to 2,1,8 isomerisation is the electron-donating character of the exopolyhedral ligands as opposed to steric crowding. We believe that this isomerisation takes place when the metallacarborane is metalated by a {Ni(tmeda)} fragment (i.e. before subsequent displacement of the tmeda by phosphite – the small amount of **9** that is isolated with **10** presumably results from ligand substitution before isomerisation). Certainly, only an electronically-driven isomerisation can explain why the unsubstituted C(H) vertex in **10** has moved to the lower pentagonal belt whilst the substituted C(C_2B_{10}) remains in the upper belt.[20]

Finally we note that these tentative conclusions drawn from the trimethylphosphite work are fully consistent with the results of the chelating diphosphine work; using the larger dppe ligand resulted in a 3,1,2 to 4,1,2 isomerisation whilst the more compact, electron-donating dmpe ligand resulted in a 3,1,2 to 2,1,8 isomerisation.

Conclusions

The factors influencing the isomerisation proceses of heteroboranes have long been the subject of keen interest. This study of the products of the metalation of singly-deboronated 1,1′-bis(*o*-carborane) with nickel-phosphine and –phosphite fragments suggests that the relief of steric crowding is important in driving the 3,1,2 to 4,1,2-NiC_2B_9 isomerisation, whereas for the alternative 3,1,2 to 2,1,8-NiC_2B_9 isomerisation the basicity of the exopolyhedral ligands appears to be key.

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Experimental

Synthesis

Experiments were performed under dry, oxygen free N_2, using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. THF and petrol were freshly distilled under nitrogen from sodium wire immediately before use whilst DCM was purified in an MBRAUN SPS-800. All solvents were degassed (3×freeze-pump-thaw cycles) before use. Deuterated solvents were stored over 4 Å molecular sieves. Preparative TLC employed 20×20 cm Kieselgel F_{254} glass plates and column chromatography

used 60 Å silica as the stationary phase. NMR spectra at 400.1 MHz (^{1}H), 162.0 MHz (^{31}P) or 128.4 MHz (^{11}B) were recorded on a Bruker DPX-400 spectrometer from $CDCl_3$, CD_2Cl_2 or $(CD_3)_2CO$ solutions, at room temperature unless otherwise stated. Electron impact mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental analyses were conducted using an Exeter CE-440 elemental analyser. The starting materials 1,1′-bis(*o*-carborane),[21] its deboronated derivative [HNMe$_3$][7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{11}$] ([HNMe$_3$]**I**),[3] [$NiCl_2$(dmpe)] [22] *cis*-[$NiCl_2(PMe_3)_2$],[23] *cis*-[$NiCl_2(PMe_2Ph)_2$],[23] *cis*-[$NiCl_2(PMePh_2)_2$] [23] and [Ni_3Cl_5(tmeda)$_3$]Cl [18] were prepared by literature methods or slight variations thereof. [$NiCl_2$(dppe)] and all other reagents were supplied commercially.

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-dppe-3,1,2-*closo*-$NiC_2B_9H_{10}$] (1) and [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-dppe-4,1,2-*closo*-$NiC_2B_9H_{10}$] (2). Salt [HNMe$_3$]**I** (0.20 g, 0.59 mmol) was dissolved in dry THF (20 mL), *n*-BuLi (0.51 mL of 2.5M solution in hexanes, 1.29 mmol) was added dropwise at 0 °C and the solution was stirred at room temperature for 2 hr. The pale yellow THF solution of Li_2[7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{10}$] was frozen at -196 °C, [$NiCl_2$(dppe)] (0.34 g, 0.64 mmol) was added and the reaction mixture stirred overnight at room temperature, during which time the solution changed to green-purple. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol (50:50) afforded a green band (R_f = 0.55) subsequently identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-dppe-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**1**) (0.089 g, 23%) and a red-purple band (R_f = 0.66) identified as [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4-dppe-4,1,2-*closo*-$NiC_2B_9H_{10}$] (**2**) (0.068 g, 15%).

1: $C_{30}H_{45}B_{19}NiP_2$ requires C 49.2, H 6.20; $C_{30}H_{45}B_{19}NiP_2{\cdot}CH_2Cl_2$ requires C 45.6, H 5.80. Found for **1**·CH_2Cl_2: C 45.8, H 5.31%. ^{11}B{^{1}H} NMR [$(CD_3)_2CO$], δ 5.9 (1B), 2.6 (1B), -2.8 (1B), -5.3 to -18.3 multiple overlapping resonances with maxima at -5.3, -8.3, -10.2, -11.5, -12.9, -14.3, -15.8, -18.3 (total integral of last eight resonances 16B). ^{1}H NMR (CD_2Cl_2), δ 7.97-7.30 (m, 20H, C_6H_5), 3.08 (s, 1H, CH_{cage}), 2.52-2.22 (m, 4H, P{CH_2}$_2$P), 1.74 (d, $^{3}J_{PH}$ = 10.0 Hz, 1H, CH_{cage}). ^{1}H{^{31}P} NMR (CD_2Cl_2), δ 7.97-7.30 (m, 20H, C_6H_5), 3.08 (s, 1H, CH_{cage}), 2.52-2.22 (m, 4H, P{CH_2}$_2$P), 1.75 (s, 1H, CH_{cage}). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$], δ 51.8 (d, $^{2}J_{PP}$ = 25.5 Hz, 1P), 41.0 (d, $^{2}J_{PP}$ = 25.5 Hz, 1P). EIMS, envelope centred on *m/z* 731.5 (M^+).

2: $C_{30}H_{45}B_{19}NiP_2$ requires C 49.2, H 6.20; $C_{30}H_{45}B_{19}NiP_2{\cdot}CH_2Cl_2$ requires C 45.6, H 5.80. Found for **2** C 45.4, H 6.19%. ^{11}B{^{1}H} NMR [$(CD_3)_2CO$], δ 4.7 (1B), -3.4 to -15.8 multiple overlapping resonances with maxima at -3.4, -4.1, -6.9, -10.6, -13.2, -15.8 (total integral of last six resonances 18B). ^{1}H NMR [$(CD_3)_2CO$], δ 7.92-7.78 (m, 8H, C_6H_5), 7.58-7.45 (m, 12H, C_6H_5), 3.95 (s, 1H, CH_{cage}), 2.85-2.70 (m, 4H, P{CH_2}$_2$P), 1.90 (s, 1H, CH_{cage}). ^{31}P{^{1}H} NMR

[$(CD_3)_2CO$], δ 63.9 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 199 K), δ 69.6 (d, $^2J_{PP}$ = 33.2 Hz, 1P), 60.6 (d, $^2J_{PP}$ = 33.2 Hz, 1P). EIMS, envelope centred on *m/z* 731.5 (M^+).

Thermal isomerisation of 1 to 2. Compound **1** (0.020 g, 0.027 mmol) was dissolved in THF (20 mL) and the solution heated at reflux for 2 hr. The solvent was removed and the product purified by preparative TLC using an eluent system of DCM:petrol (50:50) to afford a red-purple band at R_f = 0.66 identified as **2** (0.014 g, 70 %) by ^1H, ^{31}P and ^{11}B NMR spectroscopies.

[8-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-dmpe-2,1,8-*closo*-$NiC_2B_9H_{10}$] (3). Salt [$HNMe_3$]**I** (0.20 g, 0.59 mmol) was deprotonated with *n*-BuLi (0.51 mL of 2.5M solution in hexanes, 1.29 mmol) as above and then frozen at -196 °C. [$NiCl_2$(dmpe)] (0.18 g, 0.64 mmol) added and the reaction mixture stirred overnight at room temperature during which time the solution changed to orange-yellow. All volatiles were removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Following spot TLC (DCM:petrol, 50:50) purification by preparative TLC using the same eluent gave yellow-orange product (R_f = 0.44) subsequently identified as [8-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2-dmpe-2,1,8-*closo*-$NiC_2B_9H_{10}$] (**3**) (0.090 g, 35%). $C_{10}H_{37}B_{19}NiP_2$ requires C 24.8, H 7.71. Found for **3** C 23.6, H 7.79%. $^{11}B\{^1H\}$ NMR [$(CD_3)_2CO$], δ -3.6 (2B), -4.7 (1B), -6.0 (1B), -7.6 (1B), -10.6 (8B), -13.5 (2B), -16.9 (1B), -18.7 (1B), -20.3 (2B). ^1H NMR [$(CD_3)_2CO$], δ 4.29 (s, 1H, CH_{cage}), 2.39-2.12 (m, 4H, P{CH_2}$_2$P and s, 1H, CH_{cage}), 1.65-1.60 (m, 12H, CH_3). $^1H\{^{31}P\}$ NMR [$(CD_3)_2CO$], δ 4.28 (s, 1H, CH_{cage}), 2.28-2.14 (m, 4H, P{CH_2}$_2$P and s, 1H, CH_{cage}), 1.64 (s, 6H, CH_3), 1.63 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$], δ 46.2 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 203 K), δ 48.9 (d, $^2J_{PP}$ = 48.6 Hz, 1P), 45.8 (d, $^2J_{PP}$ = 48.6 Hz, 1P). EIMS, envelope centred on *m/z* 483.4 (M^+).

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-(PMe_3)$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (4) and [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-Cl-3-PMe_3-8-PMe_3-3,1,2-*closo*-$NiC_2B_9H_9$] (5). Salt [$HNMe_3$]**I** (0.20 g, 0.59 mmol) was treated with *n*-BuLi (0.51 mL of 2.5M solution in hexanes, 1.29 mmol) as above and frozen at -196 °C. *Cis*-[$NiCl_2(PMe_3)_2$] (0.18 g, 0.64 mmol) was added and the reaction mixture stirred overnight at room temperature, during which time the solution turned green. THF was removed *in vacuo* and the crude mixture was dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol, 50:50, afforded a green band (R_f = 0.50) subsequently identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-(PMe_3)$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**4**) (0.070 g, 24%). $C_{10}H_{39}B_{19}NiP_2$ requires C 24.7, H 8.10. Found for **4** C 24.4, H 8.30%. $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ 0.5 (1B), -1.4 (1B), -2.6 (1B), -4.6 (1B), -7.7 to -16.4 multiple overlapping resonances with maxima at -7.7, -10.3, -12.4, -15.4, -16.4 (total integral of last five resonances 14B), -21.8 (1B). ^1H NMR ($CDCl_3$), δ 3.99 (s, 1H, CH_{cage}), 1.64 (d, $^3J_{PH}$ = 10.8 Hz, 1H, CH_{cage}), 1.55 (d, $^2J_{PH}$ = 9.6 Hz, 9H, CH_3), 1.49 (d, $^2J_{PH}$ = 8.4 Hz, 9H, CH_3). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ 3.99 (s, 1H, CH_{cage}), 1.64 (s, 1H, CH_{cage}), 1.52 (s, 9H, CH_3),

1.47 (s, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ -9.9 (d, $^2J_{PP}$ = 43.3 Hz, 1P), -24.9 (d, $^2J_{PP}$ = 43.3 Hz, 1P). EIMS, envelope centred on *m/z* 485.3 (M^+).

A trace amount of purple band (R_f = 0.70) was also obtained, crystallisation of which revealed both purple and colourless solids, the former in sufficient amount for it to be identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3-Cl-3,8-$(PMe_3)_2$-3,1,2-*closo*-$NiC_2B_9H_9$] (**5**). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ -1.9 (1B), -3.3 (1B), -4.0 (1B), -5.3 (1B), -6.5 (1B), -8.1 to -15.2 multiple overlapping resonances with maxima at -9.6, -10.6, -12.6 (total integral of last three resonances 10B), -15.9 (1B), -17.7 (2B), -25.4 (1B). ^1H NMR ($CDCl_3$), δ 6.13 (s, 1H, CH_{cage}), 1.59 (s, 1H, CH_{cage}), 1.74 (d, $^2J_{PH}$ = 12.0 Hz, 9H, CH_3), 1.36 (d, $^2J_{PH}$ = 15.6 Hz, 9H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ -9.2 (q, $^1J_{PB}$ = 145.8 Hz, 1P), -20.7 (s, 1P). EIMS, envelope centred on *m/z* 519.9 (M^+).

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (6) and [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-10-(PMe_2Ph)-7,8-*nido*-$C_2B_9H_{10}$] (7). Salt [$HNMe_3$]**I** (0.20 g, 0.59 mmol) was treated with *n*-BuLi (0.51 mL of 2.5M solution in hexanes, 1.29 mmol) as described previously and then frozen at -196 °C. To this was added *cis*-[$NiCl_2(PMe_2Ph)_2$] (0.25 g, 0.64 mmol) and the reaction mixture stirred overnight at room temperature. All volatiles were removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol in a ratio of 40:60 afforded a green band (R_f = 0.45) subsequently identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-$(PMe_2Ph)_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**6**) (0.093 g, 25%). $C_{20}H_{43}B_{19}P_2Ni$ requires C 39.4, H 7.11. Found for **5** C 38.8, H 7.20%. $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ 1.6 (1B), -0.7 (1B), -2.4 (1B), -4.7 (1B), -8.7 to -16.2 multiple overlapping resonances with maxima at -8.7, -9.7, -12.1, -16.2 (total integral of last four resonances 14B), -21.6 (1B). ^1H NMR ($CDCl_3$), δ 7.83 (m, 2H, C_6H_5), 7.58-7.38 (m, 8H, C_6H_5), 4.00 (s, 1H, CH_{cage}), 1.74 (d, $^2J_{PH}$ = 10.0 Hz, 3H, CH_3), 1.54 (d, 3H, CH_3, signal partially obscurred by water), 1.37 (d, $^2J_{PH}$ = 8.0 Hz, 3H, CH_3), 1.18 (d, $^3J_{PH}$ = 14.0 Hz, 1H, CH_{cage}), 1.07 (d, $^2J_{PH}$ = 10.0 Hz, 3H, CH_3). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ 7.84 (m, 2H, C_6H_5), 7.58-7.38 (m, 8H, C_6H_5), 4.00 (s, 1H, CH_{cage}), 1.75 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.16 (s, 1H, CH_{cage}), 1.09 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ -4.8 (d, $^2J_{PP}$ = 39.7 Hz, 1P), -14.9 (d, $^2J_{PP}$ = 39.7 Hz, 1P). EIMS, envelope centred on *m/z* 609.3 (M^+).

A trace amount of purple band (R_f = 0.50) was also obtained, crystallisation of which revealed both purple and colourless solids, the latter in sufficient amount for it to be identified as [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-10-(PMe_2Ph)-7,8-*nido*-$C_2B_9H_{10}$] (**7**). $C_{12}H_{32}B_{19}P$ requires C 34.9, H 7.81. Found for **7** C 34.4, H 7.23%. $^{11}B\{^1H\}$ NMR [$CDCl_3$], δ -2.7 (1B), -4.9 (1B), -8.5 to -18.4 multiple overlapping resonances with maxima at -8.5, -9.8, -10.7, -13.2, -15.0, -16.4, -17.5 (total integral of last seven resonances 15B), -33.4 (1B), -34.2 (1B). ^1H NMR ($CDCl_3$), δ 7.76-7.65 (m, 5H, C_6H_5), 3.66 (s, 1H, CH_{cage}), 2.49 (s,

1H, CH_{cage}), 1.79 (d, $^2J_{PH}$ = 10.8 Hz, 6H, CH_3). ^{1}H{^{31}P} NMR ($CDCl_3$), δ 7.76-7.65 (m, 5H, C_6H_5), 3.66 (s, 1H, CH_{cage}), 2.49 (s, 1H, CH_{cage}), 1.79 (s, 6H, CH_3). ^{1}H{^{11}B} NMR ($CDCl_3$), includes δ -1.93 (br s, 1H, μ-H). ^{31}P{^{1}H} NMR ($CDCl_3$), δ -8.8 (q, $^1J_{PB}$ = 148.5 Hz). EIMS, envelope centred on *m/z* 412.7 (M^+).

[2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4,4-($PMePh_2$)$_2$-4,1,2-*closo*-$NiC_2B_9H_{10}$] (8). Salt [$HNMe_3$]**I** (0.20 g, 0.59 mmol) was deprotonated with *n*-BuLi (0.51 mL of 2.5M solution in hexanes, 1.29 mmol) as above and frozen at -196 °C. *Cis*-[$NiCl_2(PMePh_2)_2$] (0.33 g, 0.64 mmol) added and the reaction mixture stirred overnight at room temperature. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol in a ratio of 40:60 afforded an olive-green band (R_f = 0.48) subsequently identified as [2-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-4,4-($PMePh_2$)$_2$-4,1,2-*closo*-$NiC_2B_9H_{10}$] (**8**) (0.090 g, 20%). $C_{30}H_{47}B_{19}NiP_2$ requires C 49.1, H 6.46; $C_{30}H_{47}B_{19}NiP_2 \cdot CH_2Cl_2$ requires C 45.5, H 5.92; $C_{30}H_{47}B_{19}NiP_2 \cdot 0.5CH_2Cl_2$ requires C 47.2, H 6.23. Found for **6** C 47.2, H 6.91%. ^{11}B{^{1}H} NMR [$(CD_3)_2CO$], δ 5.1 (1B), -1.6 to -17.3 multiple overlapping resonances with maxima at -1.6, -3.2, -6.9, -10.4, -13.1, -15.0, -17.3 (total integral of last seven resonances 18B). ^{1}H NMR [$(CD_3)_2CO$], δ 7.73-7.67 (m, 4H, C_6H_5), 7.49-7.18 (m, 16H, C_6H_5), 4.13 (s, 1H, CH_{cage}), 2.82 (s, 1H, CH_{cage}), 1.89 [d + d (app. t), $^2J_{PH}$ = ca. 5 Hz, 5Hz, 6H, CH_3) [24]. ^{1}H{^{31}P} NMR [$(CD_3)_2CO$], δ 7.72-7.23 (m, 20H, C_6H_5), 4.11 (s, 1H, CH_{cage}), 2.81 (s, 1H, CH_{cage}), 1.89 (s, 6H, CH_3). ^{31}P{^{1}H} NMR [$(CD_3)_2CO$], δ 13.9 (s). EIMS, envelope centred on *m/z* 733.4 (M^+).

***cis*-[$NiBr_2${$P(OMe)_3$}$_2$].** By analogy with the related tris(triethylphosphite) species,[16] anhydrous $NiBr_2$ (0.50 g, 2.29 mmol) was stirred for 0.5 hr in THF (20 mL) affording a brownish-orange solution. $P(OMe)_3$ (0.54 mL, 4.58 mmol) was added to the solution which immediate changed to dark purple. The reaction mixture was stirred at room temperature for a further 2 hr. THF was removed *in vacuo* and the remaining dried under vacuum to afford a brown powder, *cis*-[$NiBr_2${$P(OMe)_3$}$_2$] (0.76 g, 71%). $C_6H_{18}Br_2NiO_6P_2$ requires C 15.4, H 3.89. Found: C 16.1, H 4.38%. ^{1}H NMR ($CDCl_3$), δ 3.87 (br. s, OCH_3). ^{31}P NMR ($CDCl_3$), δ 108.8 (br. s).

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-{$P(OMe)_3$}$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (9). Salt [$HNMe_3$]**I** (0.15 g, 0.45 mmol) was lithiated with *n*-BuLi (0.36 mL of 2.5M solution in hexanes, 0.90 mmol) as above and frozen at -196 °C. [$Ni_3(tmeda)_3Cl_5$]Cl (0.11 g, 0.15 mmol) was added and the reaction mixture allowed to stir to produce a greenish-blue solution. $P(OMe)_3$ (0.53 mL, 4.50 mmol) was added dropwise and the reaction mixture stirred overnight at room temperature during which the solution turned brown. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol, 50:50, afforded a purple band (R_f = 0.38) subsequently identified as [1-(1′-

1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-{$P(OMe)_3$}$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**9**) (0.045 g, 17%). $C_{10}H_{39}B_{19}NiO_6P_2$ requires C 20.7, H 6.76. Found for **9** C 20.5, H 6.93%. $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ 1.3 (1B), -0.6 (1B), -2.2 (1B), -4.6 (1B), -6.3 (1B), -9.7 to -14.0 multiple overlapping resonances with maxima at -9.7, -10.2, -13.1, -14.0 (total integral of last four resonances 13B), -18.7 (1B). ^1H NMR ($CDCl_3$), δ 4.59 (s, 1H, CH_{cage}), 3.85 [d + d (app. t), $^3J_{PH}$ = *ca*. 11.0 Hz, 11.0 Hz, 18H, OCH_3], 2.52 (d, $^3J_{PH}$ = 10.0 Hz, 1H, CH_{cage}). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ 4.58 (s, 1H, CH_{cage}), 3.87 (s, 9H, OCH_3), 3.84 (s, 9H, OCH_3), 2.52 (s, 1H, CH_{cage}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 117.4 (d, $^2J_{PP}$ = 118.2 Hz, 1P), 113.1 (d, $^2J_{PP}$ = 118.2 Hz, 1P). EIMS, envelope centred on *m/z* 581.3 (M^+).

[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-{$P(OMe)_3$}$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (9) and [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2,2-{$P(OMe)_3$}$_2$-2,1,8-*closo*-$NiC_2B_9H_{10}$] (10). Salt [$HNMe_3$]**I** (0.20 g, 0.59 mmol) was lithiated with *n*-BuLi (0.47 mL of 2.5M solution in hexanes, 1.18 mmol) as above and frozen at -196 °C. [Ni_3(tmeda)$_3Cl_5$]Cl (0.22 g, 0.30 mmol) was added and the reaction mixture allowed to stir for 2 hr at room temperature to produce a greenish-blue solution. $P(OMe)_3$ (0.70 mL, 5.90 mmol) was added dropwise to the solution and the reaction mixture stirred overnight at room temperature during which the solution turned brown. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through Celite®. Preparative TLC using an eluent system of DCM and petrol (50:50) afforded a purple band (R_f = 0.36) identified spectroscopically as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-3,3-{$P(OMe)_3$}$_2$-3,1,2-*closo*-$NiC_2B_9H_{10}$] (**9**) (0.010 g, 3%) and a yellow band (R_f = 0.46) subsequently identified as [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-2,2-{$P(OMe)_3$}$_2$-2,1,8-*closo*-$NiC_2B_9H_{10}$] (**10**) (0.026 g, 13%).

10: $C_{10}H_{39}B_{19}O_6NiP_2$ requires C 20.7, H 6.76. Found for **10**: C 20.3, H 6.84%. $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ -2.5 (1B), -5.6 (2B), -8.2 to -9.8 multiple overlapping resonances with maxima at -8.2, -9.8 (total integral of last two resonances 8B), -13.2 (4), -17.6 (2B), -18.4 (2B). ^1H NMR ($CDCl_3$), δ 4.32 (s, 1H, CH_{cage}), 3.83 (d with additional structure, $^3J_{PH}$ = *ca*. 10.4 Hz, 9H, OCH_3), 3.79 (d with additional structure, $^3J_{PH}$ = *ca*. 10.4 Hz, 9H, OCH_3), 2.23 (s, 1H, CH_{cage}). $^1H\{^{31}P\}$ NMR ($CDCl_3$), δ 4.31 (s, 1H, CH_{cage}), 3.83 (s, 9H, OCH_3), 3.79 (s, 9H, OCH_3), 2.22 (s, 1H, CH_{cage}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 125.2-123.5 (m, overlapping of two doublets, 1P each). EIMS: envelope centred on *m/z* 580.3 (M^+).

Crystallography

Diffraction-quality crystals of all compounds were obtained by solvent diffusion at -30 °C as follows (compound, solvent, antisolvent): **1** & **6**, THF, petrol; **2-4** & **9**, DCM, petrol; **5** & **7**, $CHCl_3$, petrol; **10**, $CDCl_3$, petrol. Compound **1** was also crystallised from DCM/petrol to yield crystals of the solvate **1**·DCM with cell dimensions *a* = 10.1148(8), *b* = 21.057(2), *c* = 11.1877(9) Å, β = 113.814(4)°, space group $P2_1$. Data from this crystal afforded a structure

which was sub-publication quality but which nevertheless confirmed the ratio of nickelacarborane to DCM allowing the microanalytical results to be rationalised.

Intensity data for were collected on a Bruker X8 APEXII diffractometer using Mo-K_α *X*-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K (200 K in the case of compound **5**) by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.[25] Using OLEX2 [26] structures were solved with the OLEX2.solve programme [27] (SHELXT [28] for compound 10) and refined by full-matrix least-squares (SHELXL).[29]

Cage C atoms not involved in the intercage link were identified by a combination of (i) the examination of refined (as B) isotropic thermal parameters, (ii) the lengths of cage connectivities, (iii) the *Vertex-Centroid Distance Method* [30] and (iv) the *Boron-H Distance Method*,[31] with all four methods affording excellent mutual agreement.

All crystals were single except for **6** and **9**, both two-component twins. Compounds **5**, **7** and **8** are free of solvate and fully ordered. In **1** the nickelacarborane is fully ordered but there is disordered solvent in the lattice that was impossible to model satisfactorily (only a fragment of THF could be identified). Hence for this structure the intensity contribution of the disordered solvent was removed using the BYPASS procedure [32] implemented in OLEX2. The total electron count of solvent per cell was 190 e which corresponds to approximately four THF plus 0.5 hexane molecules. These disordered solvent molecules predominantly occupy two voids of *ca*. 400 Å^3 each. The same procedure was also implemented for **4**: total electron count of solvent per cell 123 e, *ca.* three CH_2Cl_2 per cell in two voids of *ca*. 209 Å^3 each.

The nickelacarboane in **2** is also ordered but there is one disordered molecule of CH_2Cl_2 of solvation per asymmetric unit, however in this case the disorder was modelled. In **3** there is partial disorder of the C_2B_{10} cage involving vertices 2′ (mainly C) and 3′ (mainly B) and also disorder of P2, the CH_2CH_2 bridge of the dmpe ligand and the C211H_3 group. In both compounds **4** and **6** there is C/B disorder in the nickelacarborane cage involving vertices 2 (mainly C) and 4 (mainly B). In the case of **4** this was successfully modelled with refining but tied site occupation factors (SOFs), but such an approach was not possible for **6** (the data set is comparatively poor) and fixed SOFs of 0.85 C + 0.15 B at vertex 2 and 0.15 C + 0.85 B at vertex 4 were used. Finally, in **10** the C23 methyl group is disordered with two sets of H atoms with SOFs of 0.51(2) and 0.49(2).

For all structures H atoms bound to cage B or C atoms, including the μ-H atom in compound **7**, were allowed to refine positionally whilst other H atoms were constrained to idealised geometries; C_{phenyl}–H = 0.95 Å, C_{methyl}–H = 0.98 Å, $C_{methylene}$–H = 0.99 Å. All H displacement parameters, U_{iso}, were constrained to be 1.2×U_{eq} (bound B or C) except Me H atoms [U_{iso}(H) = 1.5×U_{eq} C(Me)]. Table 1 contains further experimental details.

<Table 1 near here>

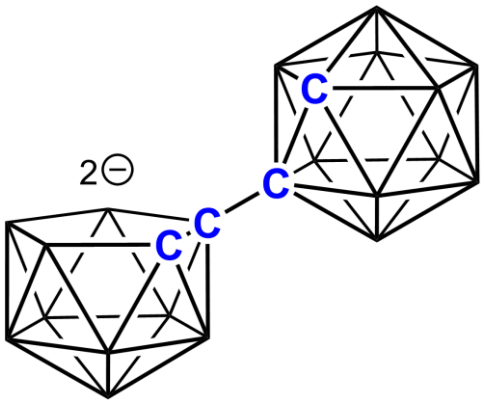


Fig. 1 The [7-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-7,8-*nido*-$C_2B_9H_{10}$]$^{2-}$ dianion (abbreviated [**I**-H]$^{2-}$ in text).

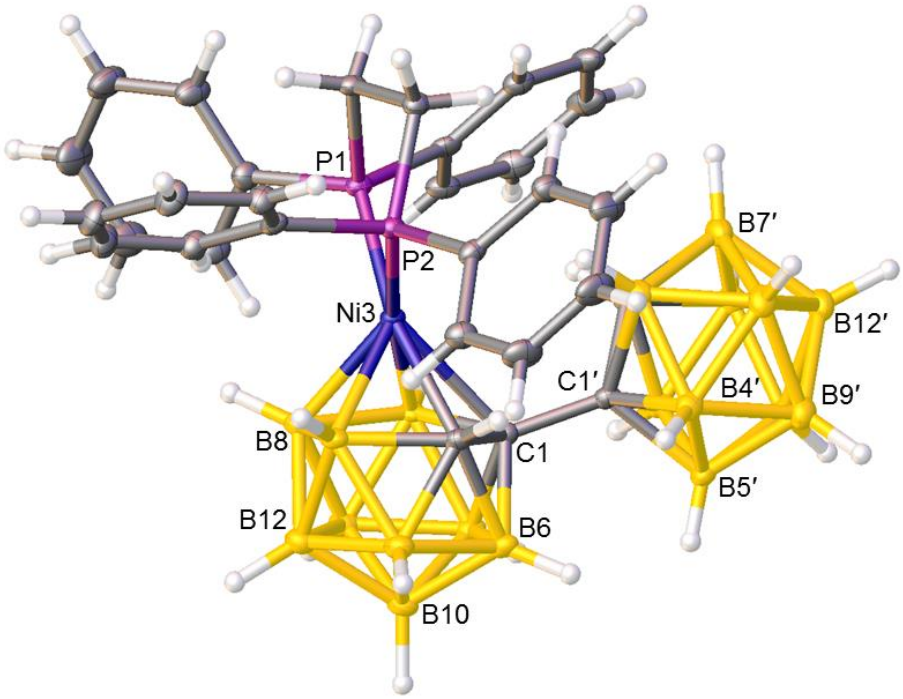


Fig. 2 Perspective view of compound **1** with atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level except for H atoms.

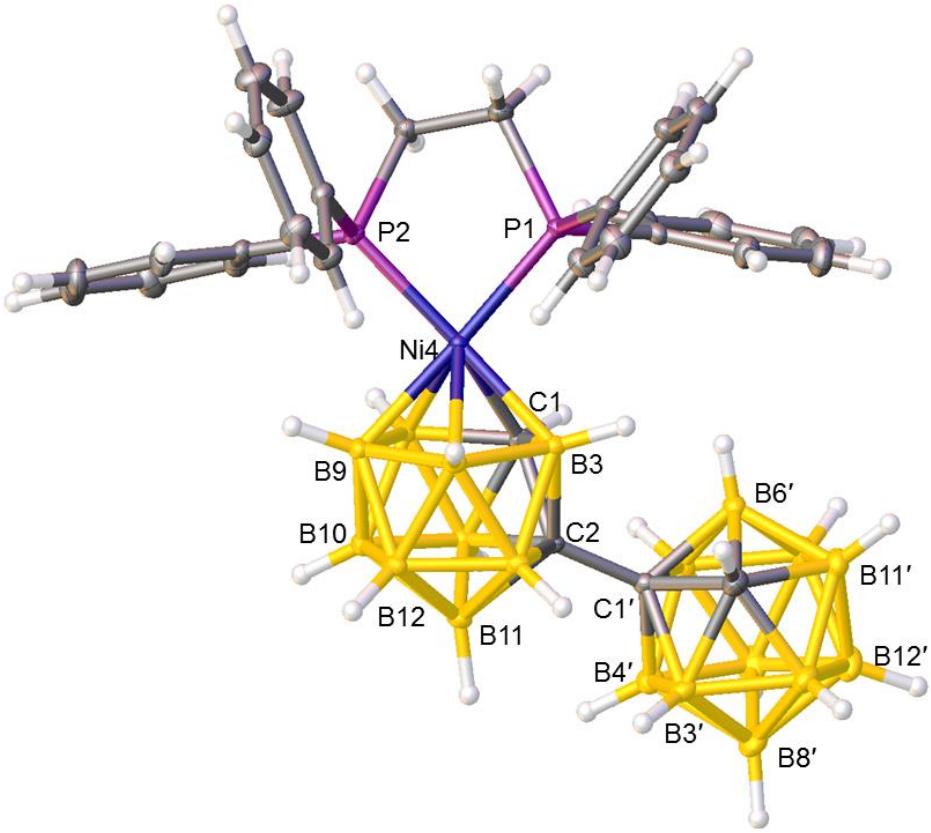


Fig. 3 Perspective view of compound **2** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

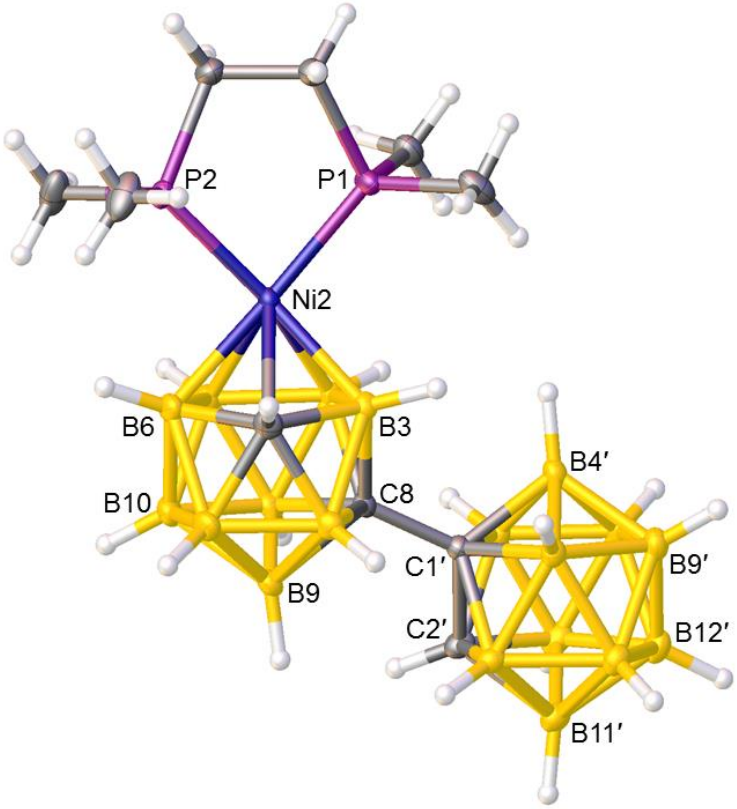


Fig. 4 Perspective view of compound **3** with atomic numbering scheme. Only the major components of the partial disorder are shown. Displacement ellipsoids as in Fig. 2.

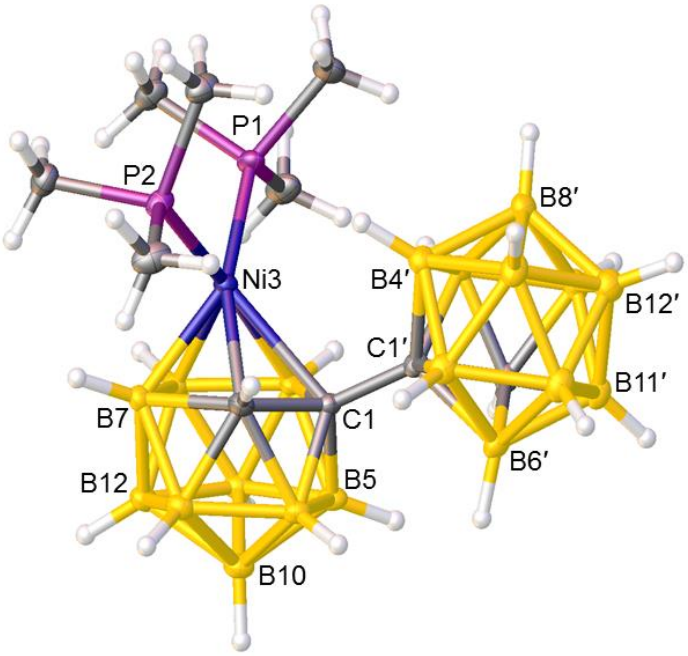


Fig. 5 Perspective view of compound **4** with atomic numbering scheme. Only the major components of the partial disorder are shown. Displacement ellipsoids as in Fig. 2.

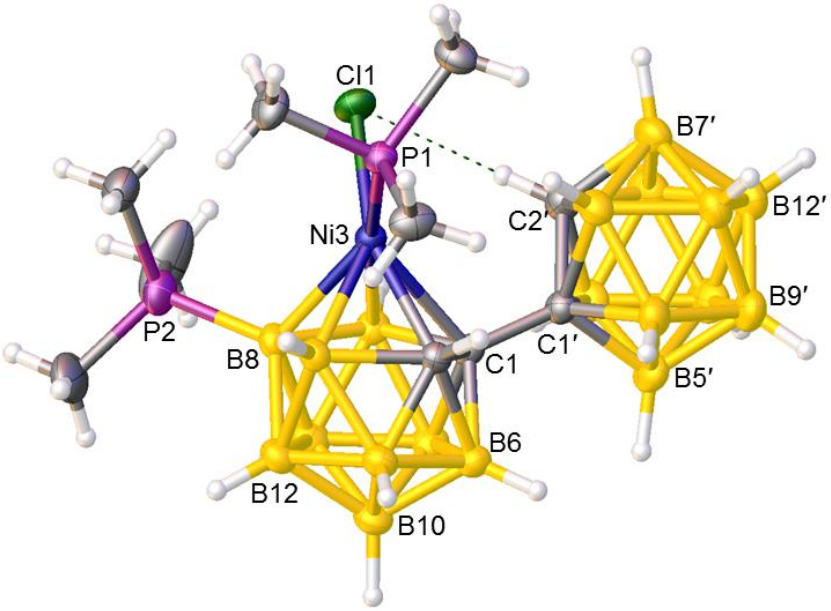


Fig. 6 Perspective view of compound **5** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

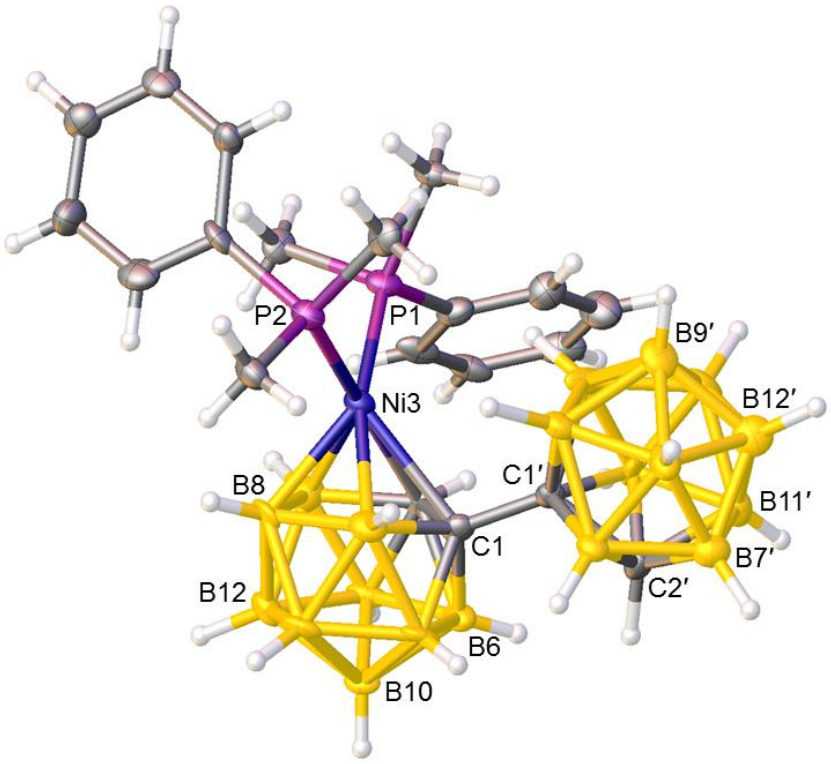


Fig. 7 Perspective view of compound **6** with atomic numbering scheme. Only the major components of the partial disorder are shown. Displacement ellipsoids as in Fig. 2.

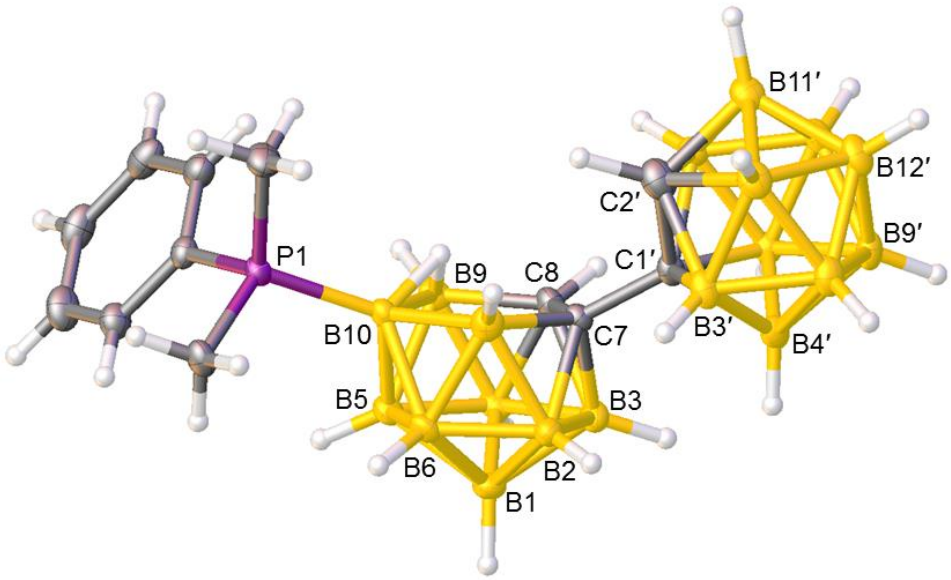


Fig. 8 Perspective view of compound **7** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

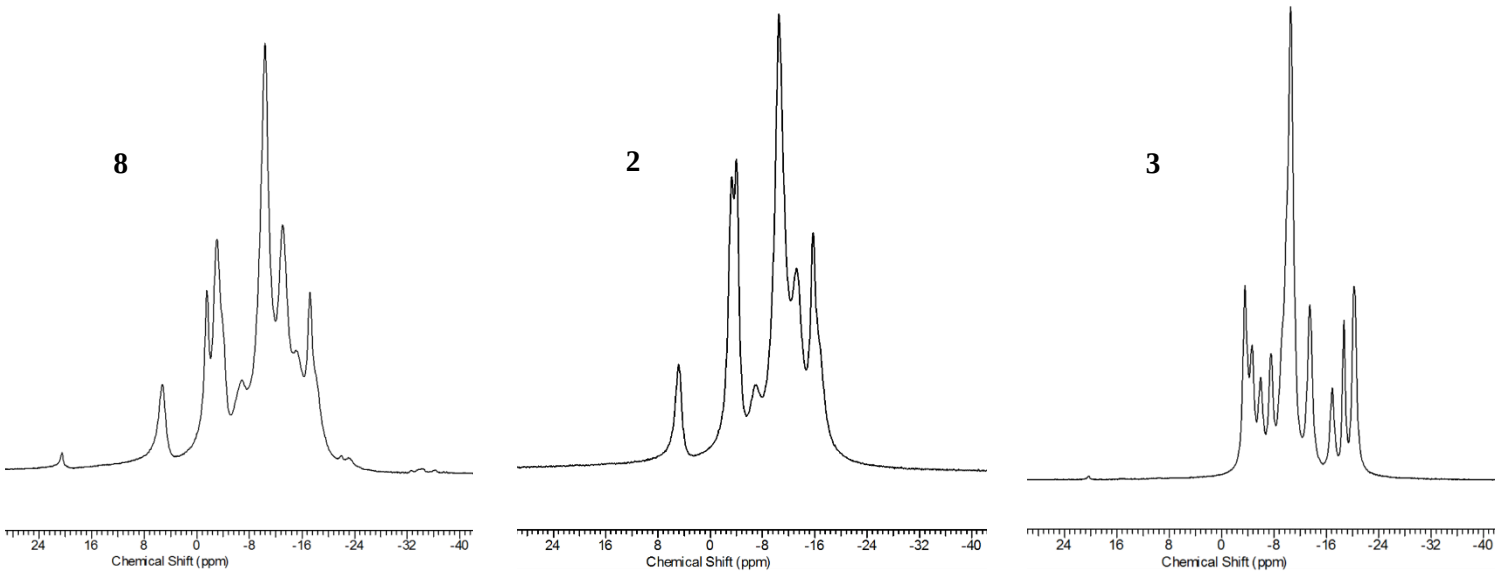


Fig. 9 Comparison of the $^{11}B\{^{1}H\}$ NMR spectra of compound **8**, **2** and **3** between +28 and –40 ppm.

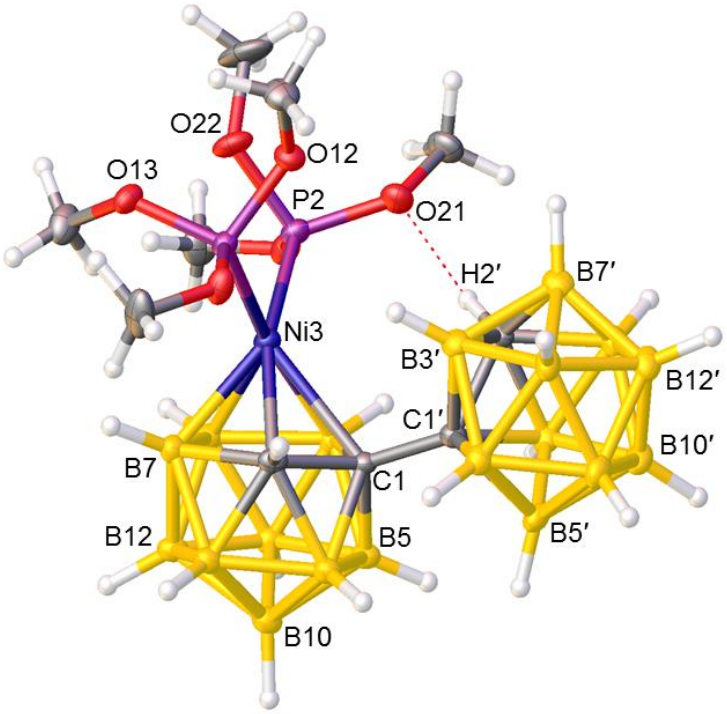


Fig. 10 Perspective view of compound **9** with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

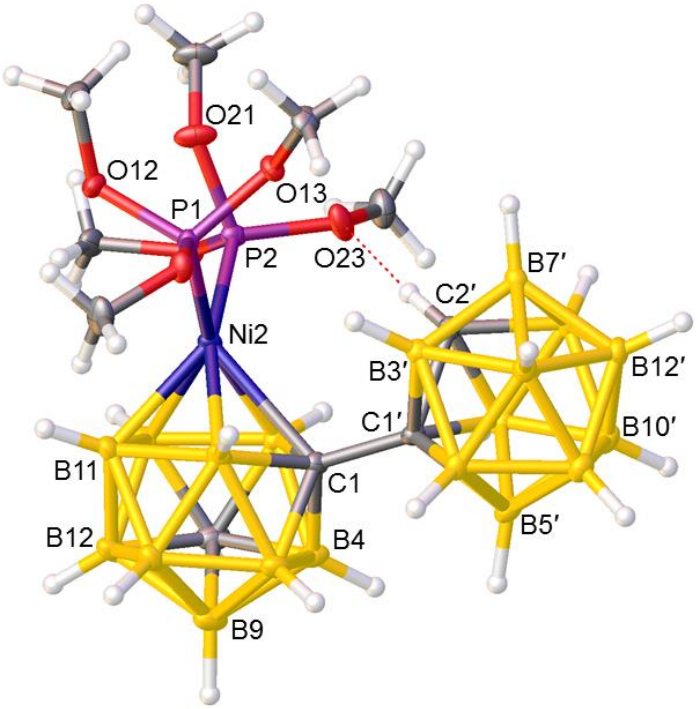
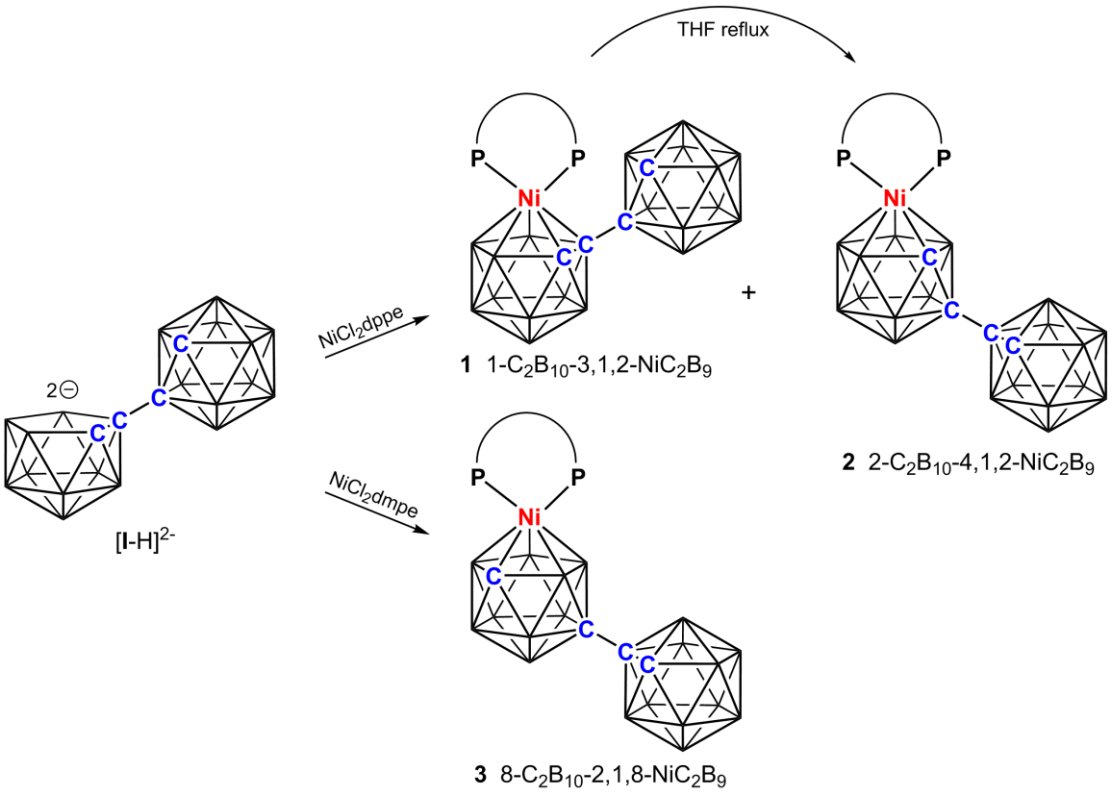
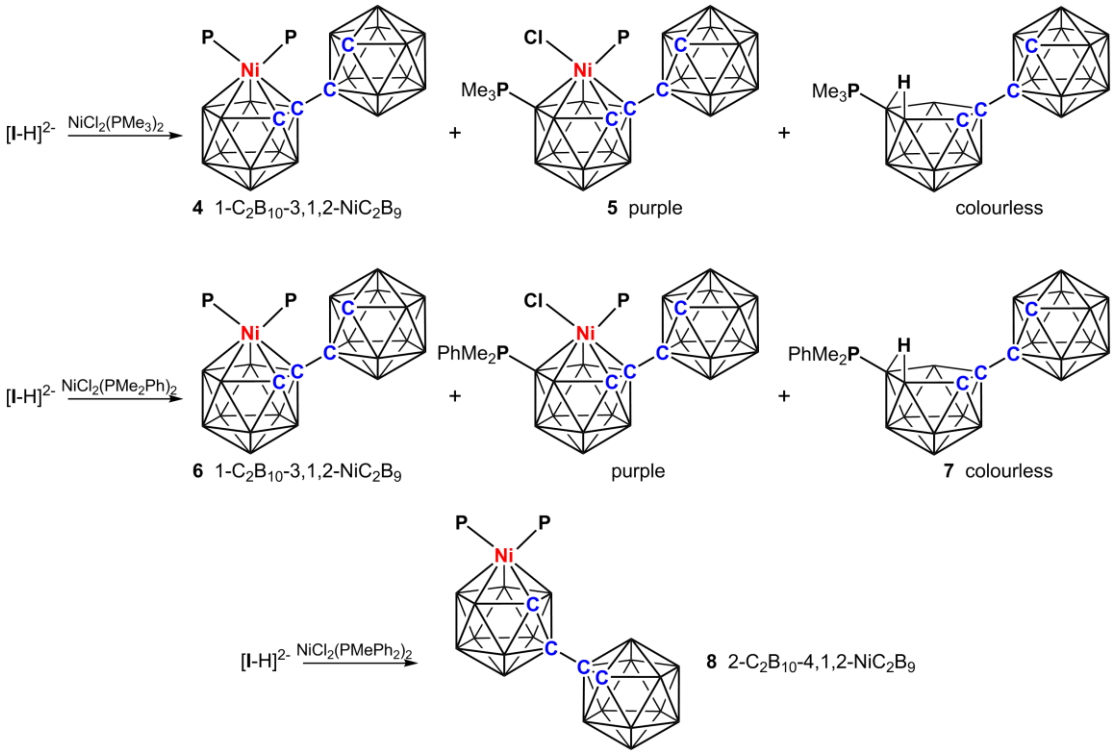


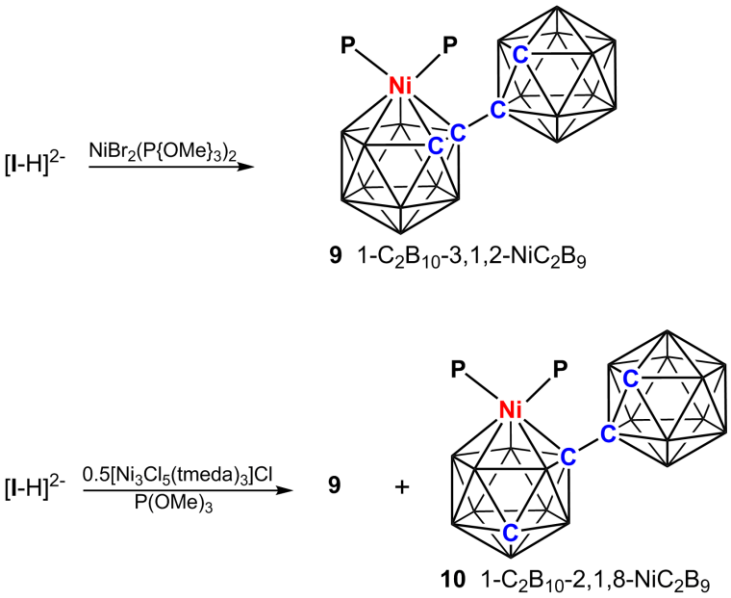
Fig. 11 Perspective view of compound **10** with atomic numbering scheme. Only the major component of the disordered $C23H_3$ group is shown. Displacement ellipsoids as in Fig. 2.



Scheme 1 Reaction between [**I**-H]$^{2-}$ and [$NiCl_2$PP] (PP = chelating diphosphine).



Scheme 2 Reaction between [**I**-H]$^{2-}$ and [$NiCl_2P_2$] (P = monodentate phosphine).



Scheme 3 Reaction between [**I**-H]$^{2-}$ and sources of the {Ni[P(OMe)$_3$]$_2$}$^{2+}$ fragment.

Table 1 Crystallographic data.

	1	**2**	**3**	**4**
Formula	$C_{30}H_{45}B_{19}NiP_2 \cdot C_{4.75}H_{9.75}O$	$C_{30}H_{45}B_{19}NiP_2 \cdot CH_2Cl_2$	$C_{10}H_{37}B_{19}NiP_2$	$C_{10}H_{39}B_{19}NiP_2 \cdot C_{0.75}H_{1.5}Cl_{1.5}$
M	814.57	816.62	483.49	549.14
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	*P*bar1	*P*bar1	$P2_1/n$
a/Å	15.9009(8)	10.2951(8)	9.0457(7)	10.3294(7)
b/Å	15.8294(8)	13.7359(10)	12.1143(10)	29.295(2)
c/Å	18.1091(8)	16.4159(13)	13.0918(11)	10.5038(7)
α/º	90	70.135(4)	112.101(4)	90
β/º	109.606(2)	74.434(4)	97.903(4)	116.545(3)
γ/º	90	74.312(4)	99.226(4)	90
U/Å^3	4293.8(4)	2061.6(3)	1280.96(18)	2843.4(4)
Z, *Z′*	4, 1	2, 1	2, 1	4, 1
F(000)/e	1697	840	500	1134
D_{calc}/Mg m^{-3}	1.260	1.315	1.254	1.134
μ(Mo-K$_\alpha$)/mm^{-1}	0.557	0.704	0.883	0.940
θ_{max}/º	28.08	33.99	28.33	27.77
Data measured	71344	59426	21467	48075
Unique data, *n*	10294	16558	6101	6682
R_{int}	0.0994	0.0417	0.0328	0.0575
R, wR_2 (obs. data)	0.0429, 0.0974	0.0436, 0.0999	0.0342, 0.0759	0.0348, 0.0847
S (all data)	0.969	1.030	0.980	1.072
Variables	532	572	384	359
E_{max}, E_{min}/e Å^{-3}	0.37, –0.71	1.23, –0.89	0.76, –0.62	0.35, –0.30
Flack parameter				

Table 1 contd.

5	**6**	**7**	**9**	**10**
$C_{10}H_{38}B_{19}ClNiP_2$	$C_{20}H_{43}B_{19}NiP_2$	$C_{12}H_{32}B_{19}P$	$C_{10}H_{39}B_{19}NiO_6P_2$	$C_{10}H_{39}B_{19}NiO_6P_2$
519.89	609.58	412.73	581.45	581.45
monoclinic	monoclinic	monoclinic	triclinic	triclinic
$P2_1/n$	$P2_1$	$P2_1/c$	*P*bar1	*P*bar1
11.2413(5)	9.8159(13)	7.0021(9)	11.0321(11)	10.2399(12)
13.8817(6)	11.0792(15)	12.7125(16)	11.6703(12)	10.9998(13)
18.1169(7)	14.558(2)	26.754(3)	11.8503(11)	13.1020(15)
90	90	90	109.302(4)	78.50297)
97.664(2)	90.703(9)	95.459(3)	95.518(5)	89.803(6)
90	90	90	93.573(6)	78.700(6)
2801.9(2)	1583.1(4)	2370.7(5)	1426.1(2)	1417.1(3)
4, 1	2, 1	4, 1	2, 1	2, 1
1072	632	856	600	600
1.232	1.279	1.156	1.345	1.363
0.904	0.729	0.117	0.820	0.826
28.56	25.98	28.28	26.05	31.09
50624	17876	15432	28465	33480
7045	4833	5764	5415	8810
0.0520	0.1330	0.0548	0.0850	0.0487
0.0331, 0.0862	0.0699, 0.1353	0.0587, 0.1334	0.0419, 0.0992	0.0376, 0.0809
1.039	1.047	1.026	1.020	1.057
364	441	355	413	412
0.38, –0.30	0.53, –0.51	0.58, –0.43	0.45, –0.51	0.43, –0.58
	0.44(4)			

References

1. J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc*., 1964, **86**, 1643.
2. W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Cryst*., 2014, E**70**, 462.
3. G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair and A. J. Welch, *Dalton Trans*., 2015, **44**, 5628.
4. (a) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc*., 1972, **94**, 4882; (b) T. P. Hanusa and L. J. Todd, *Polyhedron*, 1985, **4**, 2063.
5. R. E. King, S. B. Miller, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem*., 1983, **22**, 3548.
6. Initially EHMO calculations were used to analyse both the ML_2 orientation and the related slip distortion: see (a) D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Chem. Commun*., 1977, 605; (b) *idem, J. Chem. Soc., Dalton Trans*., 1978, 1363. More recently the slip distortion was analysed at the DFT level of theory with energy decomposition analysis emphasising the importance of steric factors in this distortion: see P. D. Abram, D. McKay, D. Ellis, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Dalton Trans*., 2010, **39**, 2412.
7. E. W. Abel, J. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem*., 1984, **32**, 1.
8. (a) M. R. Churchill and K. Gold, *J. Am. Chem. Soc*., 1970, **92**, 1180; (b) N. Carr, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem*., 1994, **33**, 1666; (c) K. Fallis, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem*., 1994, **33**, 4927; (d) R. M. Garrioch, P. Kuballa, K. S. Low, G. M. Rosair and A. J. Welch, *J. Organomet. Chem*., 1999, **575**, 57; (e) M. A. Fox, J. A. K. Howard, A. K. Hughes, J. M. Malget and D. S. Yufit, *J. Chem. Soc., Dalton Trans*., 2001, 2263; (f) S. Robertson, D. Ellis, G. M. Rosair and A. J. Welch, *Appl. Organomet. Chem*., 2003, **17**, 518; (g) S. Robertson, R. M. Garrioch, D. Ellis, T. D. McGrath, B. E. Hodson, G. M. Rosair and A. J. Welch, *Inorg. Chim. Acta*, 2005, **358**, 1485; (h) W. Y. Man, G. M. Rosair and A. J. Welch, *Dalton Trans*., 2015, **44**, 15417.
9. C. R. Groom and F. H. Allen, *Angew. Chem. Int. Ed*., 2014, **53**, 662.
10. *e.g*. D. McKay, S. A. Macgregor and A. J. Welch, *Chem. Sci*., 2015, **6**, 3117.
11. J. Buchanan, E. J. M. Hamilton, D. Reed and A. J. Welch, *J. Chem. Soc., Dalton Trans*., 1990, 677.
12. L. I. Zakharkin, V. a. Olshevskaya, G. G. Zhigareva, V. A. Antonovich, P. V. Perovskii, A. I. Yanovskii, A. V. Polyakov and Yu. T. Struchkov, *Metallorg. Khim.*, 1989, **2**, 1274.
13. S. A. Jasper Jr., J. Mattern, J. C. Huffman and L. J. Todd, *Polyhedron*, 2007, **26**, 3793.

14. C. A. Tolman, *Chem. Rev*., 1977, **77**, 313.
15. L. J. Vande Griend, J. C. Clardy and J. G. Verkade, *Inorg. Chem.*, 1975, **14**, 710.
16. M. M. Lindner, U. Beckmann, W. Frank and W. Klaui, *ISRN Inorg. Chem.*, 2013, **2013**, 1.
17. (a) H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. C. S. Chem. Comm.*, 1978, 322; (b) *idem, J. Chem. Soc., Dalton Trans.*, 1985, 761.
18. D. A. Handley, P. B. Hitchcock and G. J. Leigh, *Inorg. Chim. Acta*, 2001, **314**, 1.
19. D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C14.
20. In principle we might also have expected to form a 8-C_2B_{10}-2,1,8-NiC_2B_9 species from the reaction which affords compound **10** but such a species was not isolated.
21. S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167.
22. G. Booth and J. Chatt, *J. Chem. Soc*., 1965, 3238.
23. (a) L. M. Venanzi, *J. Chem. Soc*., 1958, 719; (b) G. Booth and J. Chatt, *J. Chem. Soc*., 1960, 1718.
24. See compound **4** in R. E. King, S. B. Miller, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem*., 1983, **22**, 3548.
25. *Bruker AXS APEX2, version 2009-5*, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
26. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
27. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst*., 2015, A**71**, 59.
28. G. M. Sheldrick, *Acta Cryst.*, 2015, A**71**, 3.
29. G. M. Sheldrick, *Acta Cryst.*, 2008, A**64**, 112.
30. A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans*., 2013, **42**, 645.
31. A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans*., 2014, **43**, 5095.
32. (a) P. van der Sluis and A. L. Spek, *Acta Cryst*., 1990, A**46**, 194; (b) A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.